

Original citation:

McTurk, Euan, Amietszajew, Tazdin, Fleming, Joseph and Bhagat, Rohit (2018) *Thermo-electrochemical instrumentation of cylindrical Li-ion cells*. Journal of Power Sources, 379. pp. 309-316. doi:[10.1016/j.jpowsour.2018.01.060](https://doi.org/10.1016/j.jpowsour.2018.01.060)

Permanent WRAP URL:

<http://wrap.warwick.ac.uk/100796>

Copyright and reuse:

The Warwick Research Archive Portal (WRAP) makes this work of researchers of the University of Warwick available open access under the following conditions.

This article is made available under the Attribution-NonCommercial-NoDerivatives 4.0 (CC BY-NC-ND 4.0) license and may be reused according to the conditions of the license. For more details see: <http://creativecommons.org/licenses/by-nc-nd/4.0/>

A note on versions:

The version presented in WRAP is the published version, or, version of record, and may be cited as it appears here.

For more information, please contact the WRAP Team at: wrap@warwick.ac.uk



Thermo-electrochemical instrumentation of cylindrical Li-ion cells

Euan McTurk, Tazdin Amietszajew*, Joe Fleming, Rohit Bhagat

WMG, University of Warwick, Coventry CV4 7AL, UK

HIGHLIGHTS

- A novel in-situ thermo-electrochemical cell instrumentation method is developed.
- A range of reference electrode options is evaluated.
- Fibre optics are used to monitor temperature inside cylindrical cell's core.
- Instrumentation developed is used to measure performance of a commercial Li-ion cell.
- Cell instrumentation proposed is applicable to a wide range of cell formats.

ARTICLE INFO

Keywords:

Cell instrumentation
Optical fibres
Thermal management
Reference electrode
Safety limits
Li-ion cells

ABSTRACT

The performance evaluation and optimisation of commercially available lithium-ion cells is typically based upon their full cell potential and surface temperature measurements, despite these parameters not being fully representative of the electrochemical processes taking place in the core of the cell or at each electrode. Several methods were devised to obtain the cell core temperature and electrode-specific potential profiles of cylindrical Li-ion cells. Optical fibres with Bragg Gratings were found to produce reliable core temperature data, while their small mechanical profile allowed for low-impact instrumentation method. A pure metallic lithium reference electrode insertion method was identified, avoiding interference with other elements of the cell while ensuring good contact, enabling *in-situ* observations of the per-electrode electrochemical responses. Our thermo-electrochemical instrumentation technique has enabled us to collect unprecedented cell data, and has subsequently been used in advanced studies exploring the real-world performance limits of commercial cells.

1. Introduction

Lithium-ion cells have established themselves as the dominant family of cell chemistries for portable electronics [1], electric vehicles [2] and battery grid storage [3]. However, despite substantial improvements in energy density over the past quarter of a century, Li-ion cells remain the performance-limiting factor in the aforementioned applications. High-energy Li-ion cells suffer from high internal resistance [4], which can result in excessive temperature increases under high load or charging currents, with the possibility of the cell undergoing thermal runaway [5] and explosion. The high internal resistance also increases the overpotential of the cell, which can drive the anode and cathode potentials outside of their respective safe operating windows, resulting in capacity loss due to lithium plating and electrolyte decomposition. While these factors are well known, application of this knowledge to real-world cell design can be challenging. This is because commercial cells are hermetically sealed two-electrode systems with no internal temperature sensors and therefore no way of monitoring the

core temperature or electrode-specific potentials. As such, this usually results in the use of conservative safety limits based on full cell potential and surface temperature, which do not allow the cell's actual limits to be fully exploited. Therefore, a number of cell instrumentation techniques were trialled on commercial 18650 cylindrical cells in an attempt to obtain individual anode and cathode potentials and *in-situ* core temperature profiles, with minimal impact on the electrochemical characteristics of the cell.

Previous studies have investigated the incorporation of a reference electrode into cylindrical cells [6–12]. While many of these have involved the fabrication of cells from scratch in the laboratory [8–10], some have involved adding reference electrodes to commercial cells [6,7,11,12]. However, the invasive nature of the insertion techniques risks either damaging the cell or changing its performance characteristics. Drilling into the core of the cell [11] can cause a short circuit by leaving metal burrs from the cell can in the core, or directly damaging the electrode jellyroll if the drill bit is imperfectly aligned. Adding more electrolyte to the cell [12] lowers its internal resistance [13], and thus

* Corresponding author.

E-mail address: T.Amietszajew@warwick.ac.uk (T. Amietszajew).

alters its electrochemical performance limits and behaviour. If the electrolyte in question does not match the original contents of the cell, this can result in the formation of a different Solid Electrolyte Interphase (SEI) vs. that formed in an unmodified cell [13], which can further alter the electrochemical characteristics of the cell. Another study submerged an opened cylindrical cell into a vessel of electrolyte next to a reference electrode [7], which not only exacerbates the previous issue, but also affects the accuracy of the measured potential profiles due to the increased distance between the reference electrode and the jellyroll. Therefore, building on from previous success with the instrumentation of commercial pouch cells [14], we attempted to apply this minimally invasive electrochemical instrumentation technique to the more challenging cylindrical cell format, and developed further modification techniques that were tailored to this specific application.

Core temperature sensing in cylindrical cells has previously involved the use of thermocouples [15–20], which measure only a single temperature point and are incapable of multiplexing onto a single wire; are subject to electrical interference; are a spark risk due to current carrying wires; can adversely impact the cell performance unless properly insulated; and require a cold junction element and extra calibration since they measure relative changes in temperature. This study pioneers the use of optical fibres utilising Fibre Bragg Grating (FBG) for cell temperature measurements which, by virtue of having no current carrying components, bypass the issues mentioned above. The use of optical fibres paves the way for multipoint temperature measurements using a single sensing element, as a number of FBGs can be placed on a single thread, providing multiple temperature measurement points using a single low-profile non-electrical sensor. Here, we will focus on obtaining accurate temperature profiles of a cell core using a single FBG on the optical fibre to prove that FBGs can be employed successfully in this application.

In this work we describe the approach and methodology leading to a fully thermo-electrochemically instrumented Li-ion cell. The instrumentation devised here offers an unprecedented view of the internal cell thermodynamics, enabling assessment of real thermal and electrochemical performance limitations. An array of modification techniques is illustrated in detail, offering a solution to the lack of understanding of the *in-situ* operating parameters of Li-ion cells. This is of importance to researchers and engineers working on current and new cell generations, enabling significant performance improvements without jeopardising safety.

2. Experimental

The cells considered in this study are high-energy commercial 18650s based on nickel cobalt aluminium (NCA) chemistry. Prior to modification, all cells were discharged to their minimum operating voltage of 2.5 V as specified by the manufacturer, and transferred to an argon glove box with O₂ and H₂O concentrations below 0.1 ppm. Reference electrodes and optical fibre sensors were prepared in advance, and the cells were modified according to one of the following techniques as described below and shown in Figs. 1 and 2.

2.1. FBG core temperature sensor

The FBG sensors used in this study for temperature measurements are based on raw silica fibres connected to a Yokogawa AQ6370 spectrum analyser, a three-port optical circulator (Thor Labs) and an optical coupled laser source with a nominal broadband light spectrum of 1525–1590 nm as the data transmission method. When sensing temperature using an optical fibre, ultraviolet light is used to etch an FBG onto the fibre. The FBG consists of a periodic pattern of etching of a given distance apart, i.e. a grating. Once etching is complete and the optical fibre has been inserted into the cell, light from the broadband light source is injected down the fibre via the three-port optical coupler. The FBG is transparent to most of the broadband light, but reflects a

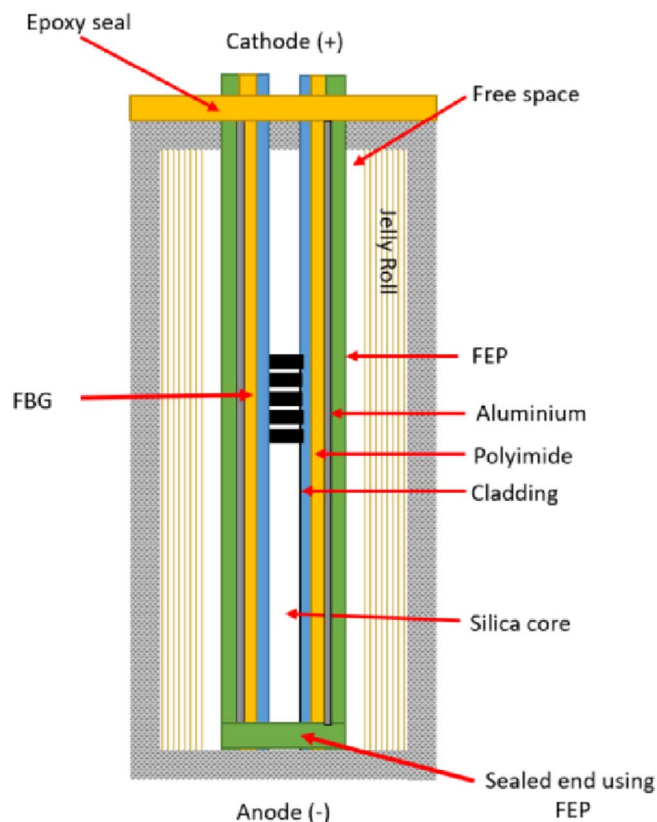


Fig. 1. Optical fibre assembly detail.

small portion of light back up the fibre; this frequency band is then detected by the spectrum analyser. The reflected light combines to produce the strongest signal at a wavelength that is equal to double the distance between the gratings, known as the Bragg wavelength and defined in Equation (1):

$$\lambda_{\text{Bragg}} = 2n\Lambda \quad [1]$$

where λ_{Bragg} is the Bragg wavelength, n is the refractive index and Λ is the space between the Bragg gratings. Changes in temperature or mechanical strain on the fibre cause the distance between the gratings to alter, resulting in a change in the FBG's refractive index, which in turn causes a change in the Bragg wavelength of light reflected back up the optical fibre. Since λ_{Bragg} is dependent on Λ , multiple FBGs with unique spacings between their gratings can be used on a single fibre. It can be seen from Equation (1) that there is a linear relationship between the Bragg wavelength of the FBG and its temperature or mechanical strain. However, differentiating between these two parameters can be challenging. This can be resolved in two ways. One approach is to exclude the unwanted strain or temperature effect by eliminating the response in the sensing element itself, e.g. by adding strain relief. An alternative solution is to incorporate a second FBG sensor in near proximity that is isolated from the disturbance in question, then subtract the difference in wave shift from the first FBG sensor [21]. The FBGs used in this study have a manufacturer-specified temperature conversion factor of 11 p.m./°C.

The FBG sensors evaluated in this work were Single Mode SMF-28 9/125 µm fibres sealed with cladding and a polyimide recoat during manufacture, which provided temperature stability in the range of -270 °C to 300 °C. However, optical fibres in their bare form would also be exposed to corrosive chemicals present in Li-ion cells, leading to fibre degradation. Therefore, the fibres were sealed in an outer skin of 1.6 mm diameter fluorinated ethylene propylene (FEP) sleeving to prevent the fibre from being affected by the electrolyte solution present

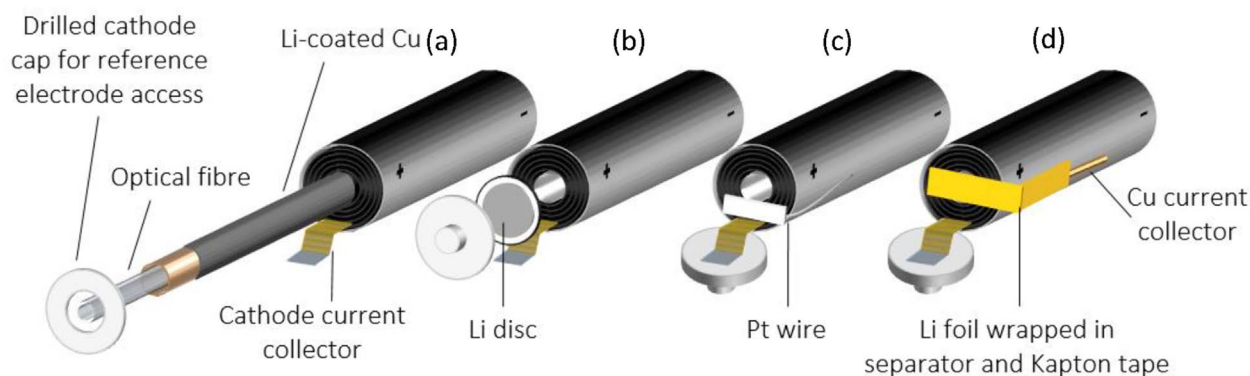


Fig. 2. Illustration of the instrumentation techniques used in this study, namely the 2-in-1 thermo-electrochemical sensor (a), Li disc (b), Pt wire (c) and Li tongue (d).

inside the Li-ion cell whilst still being able to fit inside the 2 mm diameter core of the jellyroll. A length of FEP was previously immersed in electrolyte solution for two weeks to assess its chemical resistance – no degradation was observed. Since the thermal expansion of the FEP film would impose strain on the fibre, the fibre was inserted into a 0.5 mm diameter tube of aluminium (Albion Alloys) used as strain relief prior to being given an FEP outer skin. Fig. 1 shows the complete diagram of the custom fibre assembly as incorporated into a cylindrical cell.

Each prepared FBG sensor was incorporated into the cathode cap from an 18650 cell via a hole drilled in the middle of the cap using a pillar drill, thus allowing the optical fibre to exit the cell. The opening was subsequently sealed using a silicon sealant. During the cell modification, the cell's original cathode cap was removed using a ceramic pipe cutter. The cathode current collector was cut from the cap and slung over the side of the cell. After placing the fibre sensor in the cell's mandrel core, the modified cathode cap was placed in position and sealed with Kapton tape and epoxy resin. Post-modification, the FBGs were calibrated *in-situ* in a thermal chamber to remove any influence of the residual mechanical strain on the fibre. Earlier design iterations also featured a K-type twisted pair thermocouple co-inserted with the optical fibre to support the initial temperature measurements. The results obtained using the thermally instrumented cells are shown in Fig. 3.

2.2. Li-plated Cu wire reference electrode

Bare 0.5 mm copper wire was electroplated with lithium inside the glove box following the technique outlined in Ref. [14].

The cathode cap of the cell was removed as previously described, and the stainless steel mandrel core of the cell was then removed using insulated tweezers. The Li-coated Cu wire was then placed in the mandrel core and bent at ninety degrees to allow it to exit the cell between the cathode cap and the cell can. The segment of copper wire protruding from the cell was not electroplated with lithium, thus allowing it to be used as a reference sense connector when connecting the cell to a potentiostat. The cathode cap was then replaced and adhered to the can with PTFE tape and epoxy resin.

2.3. 2-in-1 thermo-electrochemical sensor

A hybrid sensor based on the above two instrumentation procedures was developed. This consisted of an FBG optical sensor, insulated as per Section 2.1, inserted into a 2 mm diameter Li-electroplated copper tube. No additional separator material was required for the reference electrode because the inner winding of the jellyroll consisted of separator, thus ensuring that the reference electrode would not short circuit against the cathode or anode. It should be noted that the insertion of the 2-in-1 thermo-electrochemical sensor into the cell did not displace any electrolyte solution because the jellyroll is wetted with electrolyte, but not flooded, and the Li-plated copper tube fills a void vacated by the

original steel tube in the core of the cell. The internal cathode current collector was slung over the side of the cell can and the cathode cap was no longer used as a terminal. The section of copper tube that touched the cathode can upon exiting the cell was insulated with PTFE tape, leaving the protruding end of copper bare so that it may be connected to the reference sense cable on the potentiostat.

2.4. Li disc reference electrode

A 12 mm diameter disc of Li foil, and a 15 mm diameter disc of cell separator recovered from an identical cell to the ones considered in this study, were cut using hole punches. The cathode cap of the cell was removed as before, and the internal cathode current collector cut at the cap end and slung over the side of the cell. The separator and Li disc were then placed on top of the jellyroll, with the cathode cap forming the reference electrode terminal when it was placed back on the cell and sealed as previously described.

2.5. Pt wire reference electrode

Platinum wire was also considered as a reference electrode in this study due to the exceptional stability of the metal [22], which prevents any other metals from oxidising it during an electrochemical reaction. Platinum wire wrapped in separator was placed on top of the jellyroll, and exited the cell in a similar manner to the Li-plated Cu wire. The cell was then sealed with PTFE tape and epoxy resin.

2.6. Li tongue reference electrode

A piece of lithium foil measuring approximately 0.7 cm × 3 cm was wrapped in separator in a dry room with a dew point below -40 °C. A copper wire current collector was attached to the open end of the lithium strip. The entire assembly was then wrapped in Kapton tape, with the exception of a small window of separator measuring approximately 0.7 cm × 0.7 cm to allow ionic contact with the top of the jellyroll. A spacer made from a roll of Kapton tape was placed on top of the wrapped foil, on the opposite side to the exposed window. The reference electrode was then transferred into the glove box and placed on top of the jellyroll of an opened cell. The length of insulated lithium was sufficient to sling outside of the cell. The cathode cap was replaced, and the cap and reference were sealed with Kapton tape and epoxy resin.

Modified cells were then cycled at 1C inside a thermal chamber at 25 °C using a Biologic VMP3 potentiostat. Cell stability and performance were subsequently compared vs. unmodified cells.

3. Results and discussion

The 2-in-1 thermo-electrochemical sensor was the first instrument to be considered in this study. As shown in Fig. 3, the FBG sensor

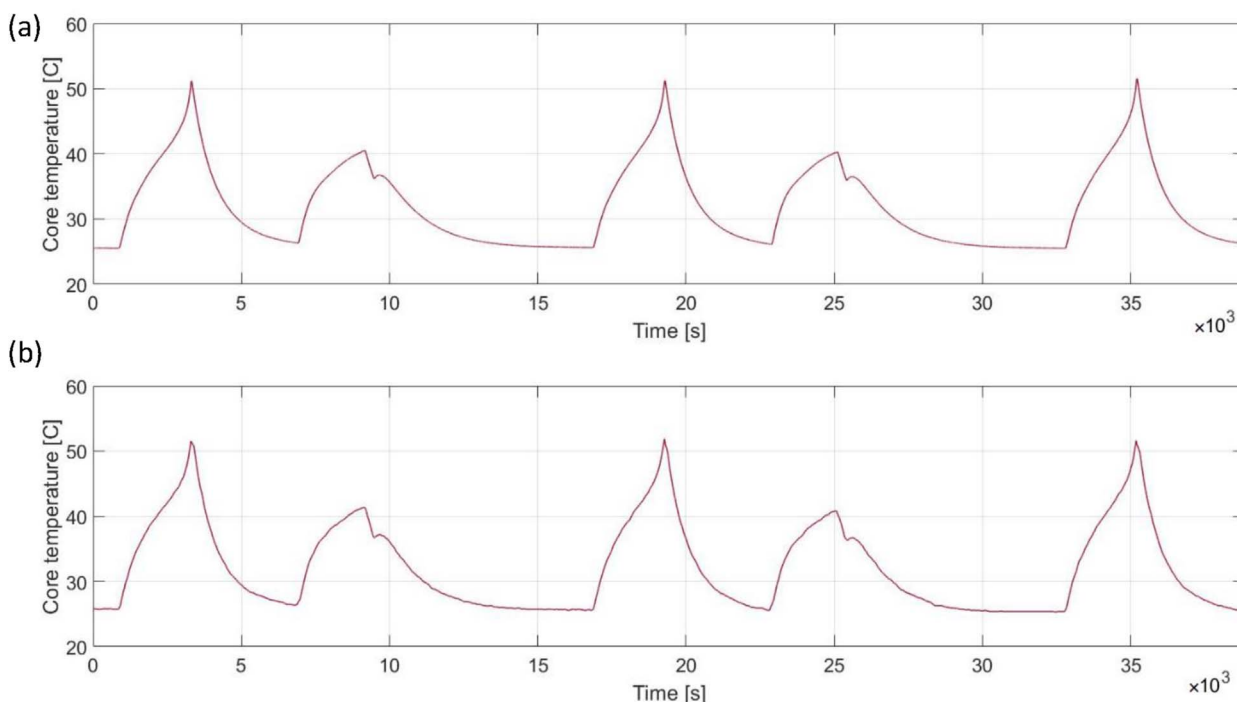


Fig. 3. Temperature profiles obtained using thermocouple (a) and fibre optic sensor (b) instrumented cell.

provided a cell core temperature profile that was in excellent agreement with readings from the K-type thermocouple that was co-inserted into the cell. Furthermore, the sealed optical fibre was not affected by the electrolyte and was able to be reused in other cells. As can be seen in Fig. 4(a) and (b), the data obtained showed that the cell core temperature was as much as 5 °C higher than the surface of the can at the end of a 1C discharge from 100% to 0% State of Charge (SoC). The same temperature differential is observed at the end of a 1.5C rapid charge from 0% SoC to V_{max} , i.e. the maximum voltage stated on the cell specification sheet. This C-rate is five times the recommended charging current stated by the manufacturer. This highlights the importance of understanding the temperature distribution throughout the cell during cycling, since any thermal limits based on the surface temperature could allow the core to exceed thermal safety limits, compromising the stability of the electrode material and leading to thermal runaway.

Following on from the successful use of a similar reference electrode insertion procedure on commercial pouch cells [14], it was expected that the modification technique would be readily transferrable to other cell formats. However, as shown in Fig. 4(c), the electrode-specific potential profiles show a marked drift over successive cycles. This issue stems in part from the location of the reference electrode in relation to the jellyroll. Only the anode faces inwards into the cell core, and the cell only contains enough electrolyte to wet the electrodes, without flooding the cell. As such, the reference electrode does not have reliable ionic contact with both the anode and cathode, which results in inaccurate potential readings. This theory was explored by using a previously reported technique [7] whereby the can is opened at the cathode end and submerged into a beaker of electrolyte with an adjacent lithium reference electrode. However, multiple attempts to use this method resulted in the submerged end of the cell can being electroplated with dendritic metallic growths and the submerged current collector being heavily corroded during cycling.

Fig. 4(d) also shows that the anode and cathode potentials recorded by a reference electrode abruptly dropped by 2 V despite the full cell potential remaining stable. This highlighted an issue with the quality of the seal formed on the insulated outer parts of the copper tube, which were insufficient to stop electrolyte from seeping underneath, establishing ionic contact with copper and thus interfering with the potential

measurements. Further studies with the Li-plated Cu wire method did not rectify either issue, and thus prompted a change in design strategy for the reference electrode.

The Li disc procedure was developed to address the issue of ionic contact with both electrodes in the cells and remove the need for selective insulation of segments of reference electrode terminal. However, as shown in Fig. 5, the electrode-specific potential profiles still drifted, with some reference electrodes completely failing after a handful of cycles. Post-mortem analysis indicated that the separator had become gelled and translucent. It transpired that the PTFE tape insulation was allowing ingress of epoxy resin, which was reacting with the separator and destroying the reference electrode. The PTFE tape was subsequently replaced with Kapton tape, since this is commonly used inside commercial cells to hold separators in place and insulate current collectors. Although this rectified the issue of epoxy resin ingress, the anode and cathode potential profiles still drifted. It was suspected that the cathode cap, made of stainless steel, may have become wetted with electrolyte and started to interfere with the electrode measurements in a similar manner to the Cu wire previously, since the cap formed the reference electrode terminal in the design. Therefore, a more stable reference electrode metal that acted as its own terminal was sourced to obtain the most reliable reference readings possible.

Fig. 5(b) shows the electrode-specific potential profiles obtained when using a platinum wire reference electrode. Despite platinum's thermodynamic stability [22], and the use of one continuous piece of metal as both the reference electrode and terminal, the voltage profiles still drifted. While some degree of change in electrode potential profiles may be expected in fresh cells due to the SEI formation process, such marked and continuous drift was not observed in the previous study concerning pouch cells. This prompted an investigation into the influence of contact pressure on measured potentials, using the Li tongue modification method.

As shown in Fig. 6(a), the Li tongue modification procedure removed the potential drift issue encountered with previous reference electrode designs. The Kapton tape spacer introduced ensured consistent and reliable ionic contact with the jellyroll, and the fact that lithium was the only metal component of the reference electrode present inside the cell guaranteed no foreign metal contamination [22].

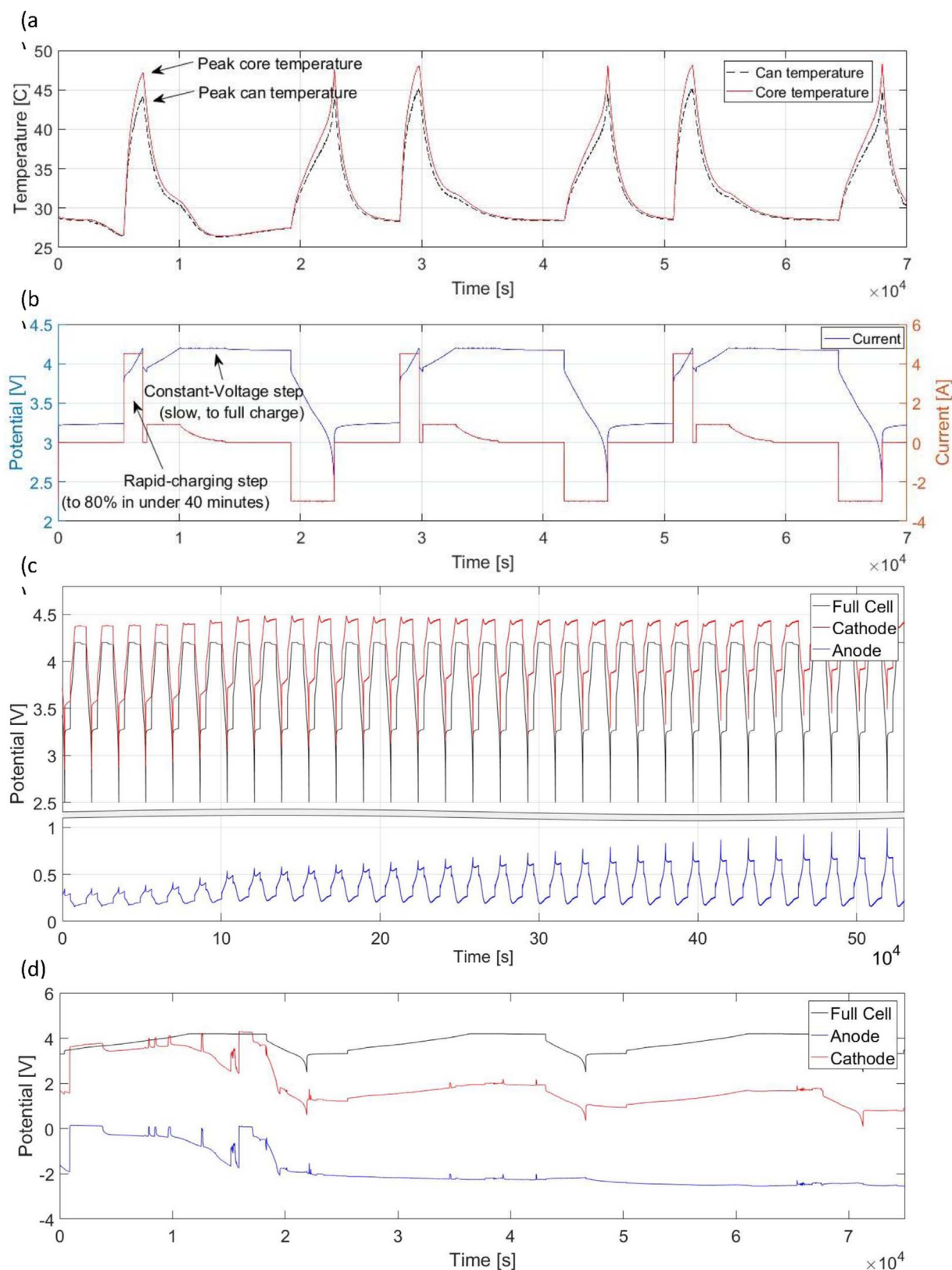


Fig. 4. Comparison of can and core temperatures recorded using a 2-in-1 thermo-electrochemical sensor (a), obtained during the rapid charging procedure for which the current and corresponding full cell voltage response are shown in (b). An example of reference electrode drift (c) and sudden failure (d) is shown.

The Kapton insulation surrounding nearly the entirety of the reference electrode also prevented the stainless steel can from shorting with the electrode and influencing the measured potentials, providing stable readings for over 50 cycles. No change in post-modification mass was

observed after cycling, thus showing that the modified cells were hermetically sealed and no electrolyte had evaporated. As shown in Fig. 6(b), the Li tongue reference electrode can be used in parallel with the FBG sensor to obtain real-time thermo-electrochemical data from

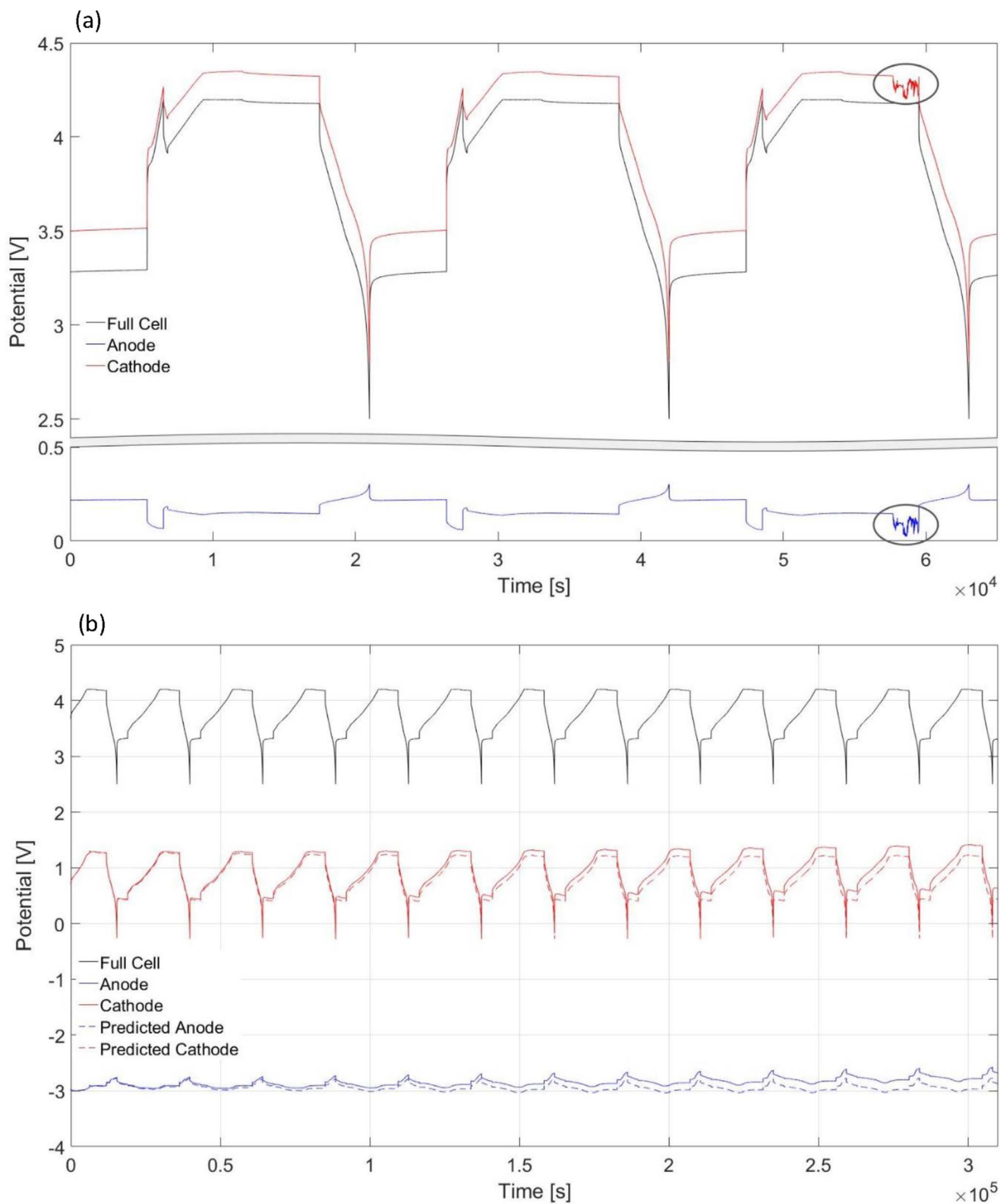


Fig. 5. Anode, cathode and full cell potential profiles of a cell with Li disc (a) and Pt (b) reference electrode. The noise in the electrode-specific potential profiles (a) as the reference electrode and separator was attacked by epoxy resin is highlighted.

the jellyroll and cell core during cycling. Finally, as illustrated in Fig. 6(c), EIS data from Li tongue cells shows that the modification procedure has no impact on the impedance of the cells, thus indicating no electrolyte leakage or other negative impacts of the modification procedure. Therefore, the procedure provides highly representative

data on cell performance vs. an unmodified cell. As the Li tongue reference electrode was proven to be the best approach in recording electrode-specific potentials, it was subsequently used for the evaluation of real performance limits of 18650 commercial cells, to be published in a separate study, showing the use of the instrumentation

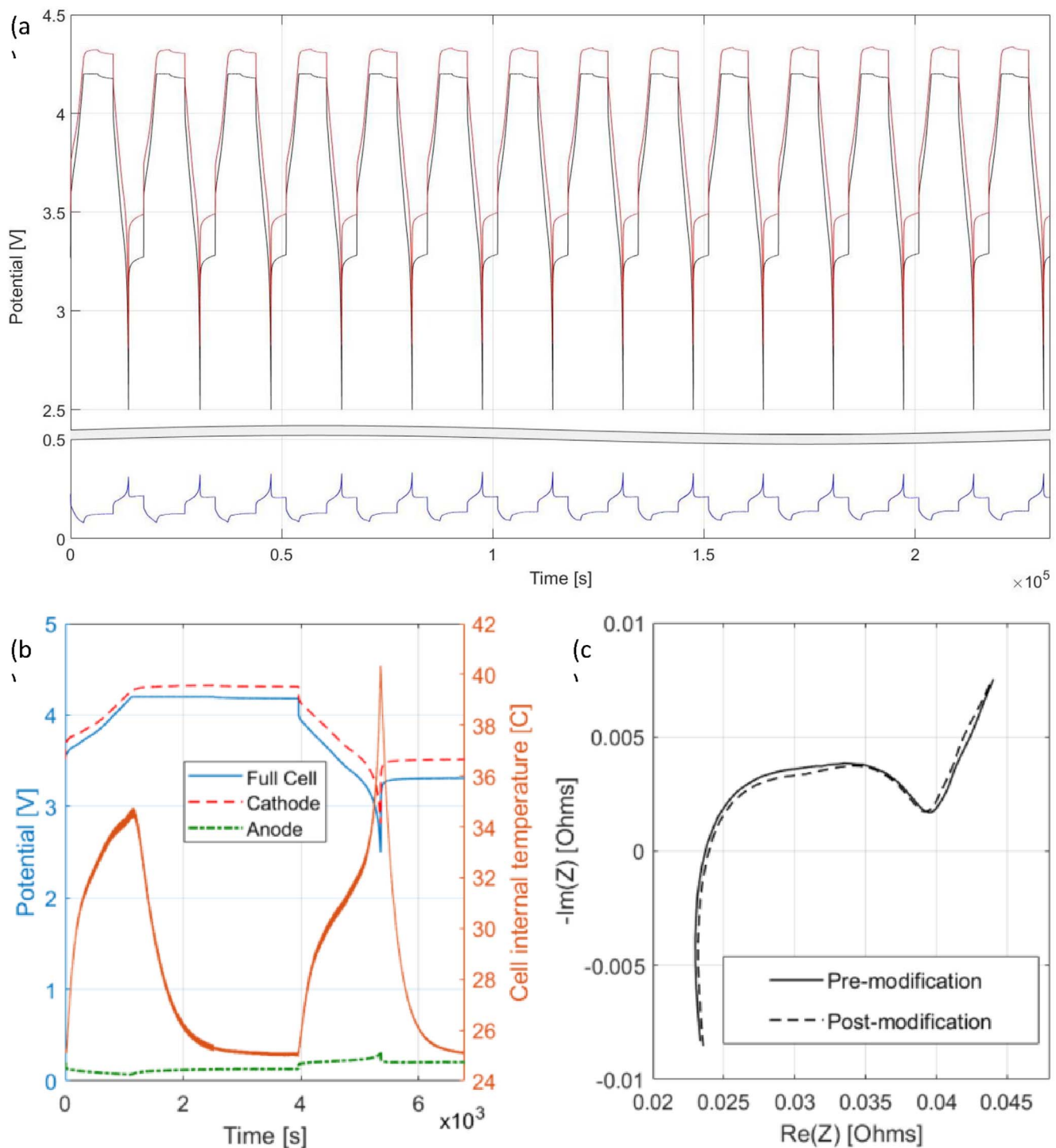


Fig. 6. The anode, cathode and full cell potential profiles for a cell fitted with the Li tongue reference electrode. No potential drift is observed (a). The ability of the Li tongue reference electrode and FBG temperature sensor to work in parallel is illustrated in (b). A Nyquist plot comparing the impedance of the cell pre- and post-modification is shown in (c).

methods developed in this work in a real-world application.

4. Conclusions

Six instrumentation techniques were devised to determine the core temperature and electrode-specific potential profiles of commercial lithium-ion cylindrical cells. The FBG optical fibre technique has proven to be a discreet and reliable method of measuring cell core temperatures, and one that can easily be scaled to include multiple temperature measurement points along the axis of the cell. The observed

temperature differential between the core and can temperature, even during relatively mild cycling conditions, provides an insight into a possible cause of uneven aging and degradation of the jellyroll across its diameter and axis, and also underlines the need to consider maximum core temperatures when specifying thermal limits based on can temperature alone. The insertion of reference electrodes into cylindrical cells highlighted the influence of ionic contact with the anode, cathode and reference electrode terminal, as well as contact pressure with the jellyroll, in obtaining stable and repeatable electrode potential profiles. The Li tongue reference electrode method managed to overcome these

obstacles and provide drift-free data for the experiments considered in this study. The thermo-electrochemical instruments developed in this study are transferrable across cylindrical and other cell formats, providing a powerful tool enabling us to unlock the full performance capability of the cell chemistries of today and tomorrow.

Author contributions

E.M-T. and T.A. performed the experiments with assistance of J.F. E.M-T., T.A. and J.F. analysed the data. R.B. supervised the project. All authors wrote the manuscript.

Competing financial interests

The authors declare no competing financial interests.

Acknowledgments

The work outlined above was carried out as part of AMPLIFII, a collaborative research project supported by Innovate UK & UK Government Office for Low Emission Vehicles (contract reference 102490). The project consortium includes the University of Warwick (coordinator), Alexander Dennis Limited, Ariel Motor Company Limited, Augean plc, Axion Consulting Limited, Delta Motorsport, HORIBA MIRA Limited, Jaguar Land Rover Limited, JCB Service, Potenza Technology Limited, Trackwise Designs Limited and the University of Oxford.

This research received funding from Jaguar Land Rover and EPSRC.

References

- [1] M. Bini, D. Capsoni, S. Ferrari, E. Quartarone, P. Mustarelli, Rechargeable Lithium Batteries, Elsevier Ltd., 2015, <http://dx.doi.org/10.1016/B978-1-78242-090-3.00001-8>.
- [2] L. Gaines, R. Cuenca, Costs of Lithium-ion Batteries for Vehicles, (2000), <http://dx.doi.org/10.2172/761281> Argonne, IL.
- [3] CEC, Environmentally Sound Management of End-of-life Batteries from Electric-drive Vehicles in North America, Commission for Environmental Cooperation, Montreal, Canada, 2015 103pp.
- [4] P.V. Braun, J. Cho, J.H. Pikul, W.P. King, H. Zhang, High power rechargeable batteries, *Curr. Opin. Solid State Mater. Sci.* 16 (2012) 186–198, <http://dx.doi.org/10.1016/j.cossms.2012.05.002>.
- [5] Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, C. Chen, Thermal runaway caused fire and explosion of lithium ion battery, *J. Power Sources* 208 (2012) 210–224, <http://dx.doi.org/10.1016/j.jpowsour.2012.02.038>.
- [6] W. Fang, O.J. Kwon, C.Y. Wang, Electrochemical-thermal modeling of automotive Li-ion batteries and experimental validation using a three-electrode cell, *Int. J. Energy Res.* 34 (2010) 107–115, <http://dx.doi.org/10.1002/er.1652>.
- [7] P. Liu, J. Wang, J. Hicks-Garner, E. Sherman, S. Soukiazian, M. Verbrugge, H. Tataria, J. Musser, P. Finamore, Aging mechanisms of LiFePO₄ batteries deduced by electrochemical and structural analyses, *J. Electrochem. Soc.* 157 (2010) A499, <http://dx.doi.org/10.1149/1.3294790>.
- [8] Y. Zhang, C.-Y. Wang, Cycle-life characterization of automotive lithium-ion batteries with LiNiO₂ cathode, *J. Electrochem. Soc.* 156 (2009) A527–A535.
- [9] G. Nagasubramanian, D.H. Doughty, 18650 Li-ion cells with reference electrode and in situ characterization of electrodes, *J. Power Sources* 150 (2005) 182–186, <http://dx.doi.org/10.1016/j.jpowsour.2005.02.024>.
- [10] Q. Wu, W. Lu, J. Prakash, Characterization of a commercial size cylindrical Li-ion cell with a reference electrode, *J. Power Sources* 88 (2000) 237–242, [http://dx.doi.org/10.1016/S0378-7753\(00\)00372-4](http://dx.doi.org/10.1016/S0378-7753(00)00372-4).
- [11] J.R. Belt, D.M. Bernardi, V. Utgikar, Development and use of a lithium-metal reference electrode in aging studies of lithium-ion batteries, *J. Electrochem. Soc.* 161 (2014) A1116–A1126, <http://dx.doi.org/10.1149/2.062406jes>.
- [12] G. Nagasubramanian, Two- and three-electrode impedance studies on 18650 Li-ion cells, *J. Power Sources* 87 (2000) 226–229, [http://dx.doi.org/10.1016/S0378-7753\(99\)00469-3](http://dx.doi.org/10.1016/S0378-7753(99)00469-3).
- [13] A. Lex-Balducci, W. Henderson, P. Stefaon, Electrolytes for lithium-ion batteries, *Lithium-Ion Batter.* Adv. Mater. Technol. (2012) 149–196, [http://dx.doi.org/10.1002/\(SICI\)1521-4095\(199804\)10:6<439::AID-ADMA439>3.0.CO;2-I](http://dx.doi.org/10.1002/(SICI)1521-4095(199804)10:6<439::AID-ADMA439>3.0.CO;2-I).
- [14] E. McTurk, C.R. Birkl, M.R. Roberts, D.A. Howey, P.G. Bruce, Minimally invasive insertion of reference electrodes into commercial lithium-ion pouch cells, *ECS Electrochem. Lett.* 4 (2015), <http://dx.doi.org/10.1149/2.0081512eel>.
- [15] N.S. Spinner, K.M. Hinnant, R. Mazurick, A. Brandon, S.L. Rose-pehrsson, S.G. Tuttle, Novel 18650 lithium-ion battery surrogate cell design with anisotropic thermophysical properties for studying failure events, *J. Power Sources* 312 (2016) 1–11, <http://dx.doi.org/10.1016/j.jpowsour.2016.01.107>.
- [16] P.J. Osswald, S.V. Erhard, J. Wilhelm, H.E. Hoster, A. Jossen, Simulation and measurement of local potentials of modified commercial cylindrical cells: I. Cell preparation and measurements, *J. Electrochem. Soc.* 162 (2015) A2099–A2105, <http://dx.doi.org/10.1149/2.0561510jes>.
- [17] T. Waldmann, M. Wohlfahrt-Mehrens, In-operando measurement of temperature gradients in cylindrical lithium-ion cells during high-current discharge, *ECS Electrochem. Lett.* 4 (2015) A1–A3, <http://dx.doi.org/10.1149/2.0031501eel>.
- [18] G. Zhang, L. Cao, S. Ge, C.-Y. Wang, C.E. Shaffer, C.D. Rahn, Situ measurement of radial temperature distributions in cylindrical Li-Ion cells, *J. Electrochem. Soc.* 161 (2014) A1499–A1507, <http://dx.doi.org/10.1149/2.0051410jes>.
- [19] C. Forgez, D. Vinh Do, G. Friedrich, M. Morcrette, C. Delacourt, Thermal modeling of a cylindrical LiFePO₄/graphite lithium-ion battery, *J. Power Sources* 195 (2010) 2961–2968, <http://dx.doi.org/10.1016/j.jpowsour.2009.10.105>.
- [20] T. Waldmann, G. Bisle, B.I. Hogg, S. Stumpp, M.A. Danzer, M. Kasper, P. Axmann, M. Wohlfahrt-Mehrens, Influence of cell design on temperatures and temperature gradients in lithium-ion cells: an in operando study, *J. Electrochem. Soc.* 162 (2015) A921–A927, <http://dx.doi.org/10.1149/2.0561506jes>.
- [21] L.W. Sommer, A. Raghavan, P. Kiesel, B. Saha, J. Schwartz, C.J. Lochbaum, A. Ganguli, A. Bae, M. Alamgir, Embedded fiber optic sensing for accurate state estimation in advanced battery management systems, *MRS Spring Meet.* 2014.
- [22] A. Lewenstam, F. Scholz, Handbook of Reference Electrodes, Springer Berlin Heidelberg, Berlin, Heidelberg, 2013, <http://dx.doi.org/10.1007/978-3-642-36188-3>.